

TITANIUM-VANADIUM-TIN COMPRISING CATALYST AND PROCESS FOR THE PREPARATION
OF PHTHALIC ANHYDRIDE

The present invention relates to a catalyst for the selective oxidation of *o*-xylene, naphthalene, or a mixture of both to phthalic anhydride in the gas-phase, using a gas
5 containing molecular oxygen, preferably air. The catalyst is characterised by a high activity and a high selectivity to phthalic anhydride. It further relates to a process for the preparation of said catalyst and a process for the production of phthalic anhydride employing said catalyst.

10 Phthalic anhydride is an important chemical intermediate used for the production of plasticizers, alkyd resins, unsaturated polyester resins and other commercial products.

The commercial production of phthalic anhydride is based on the gas phase oxidation of *o*-xylene, naphthalene, or a mixture of both. The oxidation is performed by feeding a
15 mixture of the hydrocarbon(s) and an oxygen containing gas, usually air, over a fixed bed of catalyst in a tubular reactor tube at temperatures in the range of 300–400 °C.

Commercially the oxidation is carried out in multitubular fixed-bed reactors. The reaction is exothermic and the heat of reaction is removed by cooling media, usually molten salts, circulating in the shell around the reactor tubes. In spite of the cooling, the reactor is not
20 isothermal and a temperature profile with a hot spot develops along the tube from inlet to outlet. These local hot spots are undesired because they may damage the catalyst and favour the formation of undesired side products, such as maleic anhydride, benzoic acid, carbon monoxide and carbon dioxide. In order to limit the formation of hot spots, catalyst beds with two or three different catalysts, with graduated activity, are often used. Their
25 activity is lowest at the entrance of the reactants, where most of the heat is formed, and highest at the outlet of the catalyst bed (US patent 6,362,345). The use of a highly active catalyst, especially in the lower part of the bed, i.e., near the entrance of the reactants, allows to carry out the reaction at lower temperature, with advantages for the yield of the reaction and the life of the catalyst. Therefore it has been very desirable to develop highly
30 active catalyst compositions which at the same time have a high selectivity for phthalic anhydride.

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The catalysts used today for the production of phthalic anhydride are usually supported catalysts wherein the catalytically active material is deposited, preferably as a coating, on an inert support in the form of granules or pellets, usually in the shape of spheres, cylinders or rings. The inert support in the granules or pellets of the catalyst may be, for example,
5 corundum, steatite, alumina, silicon carbide or any other material having suitable chemical inertness and mechanical and thermal stability. The amount of active material deposited on the inert carrier is usually between 1 and 15 wt.%, based on the total weight of the catalyst.

The active material of the catalysts currently being used in the production of phthalic
10 anhydride generally comprises titanium dioxide (titania), preferably having the crystalline structure of anatase, vanadium oxide, which is spread over the titanium dioxide and chemically interacts with it, and various additional components which are referred to as dopants. The dopants include elements like cesium, antimony, molybdenum, potassium, phosphorus and mixtures thereof. They are either:

- 15 (i) alkali metal or alkaline earth metal ions, the role of which is claimed to tune the surface acid-basic properties of the catalyst — alkali or alkaline earth metal ions are generally known to increase the selectivity and to decrease the activity of the catalysts (M. S. Wainwright, N. R. Foster, *Catal. Rev.-Sci. Eng.*, **19** (1979) 211; V. Nikolov, D. Klissurski, A. Anastasov, *Catal. Rev. Sci. Eng.*, **33** (1991) 319; C. R.
20 Dias, M. Farinha Portela, G. C. Bond, *Catal. Rev. Sci. Eng.*, **39** (1997) 169) — or
- (ii) transition or post-transition metal ions, the role of which is claimed to be the control of the redox properties of vanadium ions (M. S. Wainwright, N. R. Foster, *Catal. Rev.-Sci. Eng.*, **19** (1979) 211; V. Nikolov, D. Klissurski, A. Anastasov, *Catal. Rev. Sci. Eng.*, **33** (1991) 319; C. R. Dias, M. Farinha Portela, G. C. Bond,
25 *Catal. Rev. Sci. Eng.*, **39** (1997) 169); which are considered to be the main active sites in the reaction.

Another role of dopants can be the stabilization of the morphological features of titanium dioxide, such as crystallinity and surface area, or the formation of compounds with vanadium oxide having peculiar properties.

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In the oxidation of *o*-xylene or naphthalene, besides phthalic anhydride several by-products are formed, including carbon monoxide, carbon dioxide, *o*-tolualdehyde, *o*-toluic acid, phthalide, maleic anhydride and benzoic acid. In particular, these by-products are formed

- in hot spots which can develop in the reactor tubes as described above. These by-products are particularly undesired because they decrease the conversion and the yield of phthalic anhydride and some of them are difficult to remove. In commercial application, the conversion of *o*-xylene must be as high as possible and, consequently, the concentration of unconverted *o*-xylene at the reactor outlet must be as low as possible. Thus the optimal catalyst has to be as active as possible, so to achieve a very high *o*-xylene conversion, and also very selective in phthalic anhydride, leading to as low an amount as possible of by-products.
- 10 The activity of the catalysts can be increased in different ways:
- 1) Increasing the surface area of titania, so to achieve a higher dispersion of vanadium active sites (G. Centi, *Appl. Catal., A: general*, 147 (1996) 267, and references cited therein). The main drawback of this approach is that higher surface areas usually result in catalysts which are less resistant towards thermal shocks and local hot-spots, and more easily tend to exhibit recrystallization phenomena with segregation of vanadium oxide, responsible for a decrease of the surface area and progressive decrease of the activity of the catalyst.
 - 2) Loading a higher amount of vanadium oxide while keeping the surface area of titania constant (G. Centi, *Appl. Catal., A: general*, 147 (1996) 267, and references cited therein).
 - 20 The disadvantage of this approach is that it is known that an optimal amount of vanadium exists for a given titanium dioxide surface area, which corresponds to the formation of the so-called "monolayer" of active species. Higher amounts of vanadium oxide are useless and deleterious, since bulk vanadium oxide may form which does not interact with the titanium dioxide and worsens the selectivity of the catalyst towards phthalic anhydride.
 - 25 3) Using suitable dopants to improve the activity of the catalyst while maintaining good performance in terms of selectivity to phthalic anhydride (M. S. Wainwright, N. R. Foster, *Catal. Rev.-Sci. Eng.*, 19 (1979) 211; V. Nikolov, D. Klissurski, A. Anastasov, *Catal. Rev. Sci. Eng.*, 33 (1991) 319; C. R. Dias, M. Farinha Portela, G. C. Bond, *Catal. Rev. Sci. Eng.*, 39 (1997) 169). However, dopants described so far in the literature usually have negative effects on either the activity or the selectivity of the catalyst.
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Very few examples of V/Ti/O catalysts for the oxidation of *o*-xylene or naphthalene to phthalic anhydride containing tin as dopant are reported. US Patent 4,469,878 mentions the addition of tin as a promoter:

- (i) tin is added as the sole promoter to a V/Ti/O catalyst, or alternatively is added together with phosphorus;
- (ii) the amount of tin added to the catalyst composition is low: 0.1–1 wt.% of the active components, preferably 0.2–0.6 wt.%.

The performance of the catalyst is not fully satisfactory and in the examples of US Patent 4,469,878 only the oxidation of naphthalene is taken into consideration.

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It has been an object of the present invention to provide a catalyst which avoids the disadvantages of the known catalysts for the production of phthalic anhydride and has a very high activity and an excellent selectivity for the formation of phthalic anhydride, especially when *o*-xylene is used as starting material. It has been another object of the invention to provide a simple and economic process for the preparation of said catalyst starting from easily available inexpensive materials. Still another object of the invention has been to provide a process for the production of phthalic anhydride with high conversion of the starting hydrocarbon(s), high yield and high selectivity.

20 These objects have been accomplished by the catalyst according to claim 1, the process for its preparation according to claim 11 and the process for the production of phthalic anhydride according to claim 15.

Applicants have discovered that the activity of known catalysts can be significantly increased by addition of comparatively large amounts of tin, without any adverse effect on the selectivity to phthalic anhydride. A further finding of the present invention is that the addition of tin is particularly advantageous for the catalyst activity and selectivity if tin is added together with an alkali metal ion, preferably cesium.

30 The catalysts according to the invention comprise, based on the total weight of the catalytically active oxidic composition (i.e., with disregard of any inert support), from 2 to 15% by weight (calculated as V₂O₅) of vanadium and from 1 to 15% by weight (calculated as SnO₂) of tin. They further comprise from 70 to 97% by weight (calculated as TiO₂) of

titanium oxide. This means that unless there are additional components (see below), titanium oxide makes up the balance to 100%.

In a preferred embodiment, the catalyst of the invention contains, based on the catalytically active composition, up to 5% by weight (calculated as M_2O) of at least one alkali metal. Preferably, the alkali metal is lithium, potassium or rubidium, and more preferably it is cesium.

In an even more preferred embodiment, cesium is present in an amount of from 0.01 to 2% by weight (calculated as Cs_2O), based on the catalytically active composition.

In the finished catalyst, the tin is preferably present in the oxidation state +IV.

Preferably, the titanium oxide which forms the basic ingredient of the catalyst of the invention has the anatase structure and a specific surface area of 10 to 30 m^2/g , more preferably 18 to 25 m^2/g .

In a particularly preferred embodiment, the catalyst of the invention contains, based on the catalytically active composition, from 4 to 10% by weight (calculated as V_2O_5) of vanadium oxide, from 2 to 7% by weight (calculated as SnO_2) of tin oxide and from 0.1 to 0.8% by weight (calculated as Cs_2O) of cesium oxide.

In another preferred embodiment, the catalyst of the invention contains one or more element(s) selected from the group consisting of lithium, potassium, rubidium, aluminium, zirconium, iron, nickel, cobalt, manganese, silver, copper, chromium, molybdenum, tungsten, iridium, tantalum, niobium, arsenic, antimony, cerium, phosphorus, and mixtures thereof. These elements may be present in a total amount of up to 5% by weight, based on the catalytically active composition.

Advantageously, the catalyst of the invention comprises an inert support whereon the catalytically active composition is deposited in an amount of from 2 to 15%, preferably 3 to 12% by weight, based on the total weight of the catalyst including the support.

Preferably, the inert support consists of pellets or granules consisting of corundum, steatite, alumina, silicon carbide, silica, magnesium oxide, aluminium silicate, and mixtures thereof.

5 The catalyst of the present invention, which can be used in commercial multitubular reactors, may be prepared according to the following general procedure:

- 1) A mixture of the ingredients (namely: titanium oxide, vanadium oxide and tin oxide and any additional component such as cesium) of the catalyst's active composition, and/or of precursors which can be converted by thermal treatment into said ingredients
10 is prepared by dissolving, dispersing or suspending said ingredients or precursors in an aqueous or organic solvent, wherein the ingredients and/or precursors are soluble or dispersible.
- 2) If a supported catalyst shall be prepared, the above solution or suspension (slurry) is coated in the form of a thin layer on an inert support and dried or, if an unsupported
15 catalyst is desired, the solvent contained in the solution or slurry may simply be evaporated and the solid residue dried and/or comminuted, if necessary.
- 3) The coated support or solid residue obtained in the preceding step is subjected to a final thermal treatment to form the definitive active composition.

20 Suitable raw materials for the production of the catalyst include:

TiO₂ in the form of anatase of suitable surface area, preferably between 10 m²/g and 30 m²/g, more preferably between 18 m²/g and 25 m²/g;

vanadium(V) oxide or, as a precursor, any vanadium compound which can be converted by heating into vanadium(V) oxide, such as ammonium metavanadate, vanadium chlorides,
25 vanadium oxychloride, vanadium acetylacetonate and vanadium alkoxides;
tin dioxide or, as a precursor, tin compounds such as metastannic acid, orthostannic acid, tin oxyhydrates, tin chlorides (stannic or stannous) or tin acetate.

Preferred are tin compounds which are easily soluble or colloiddally dispersible in the medium employed for catalyst preparation.

30 Suitable cesium compounds include cesium sulfate, cesium nitrate, cesium chloride and any other commercial cesium salt or compound.

Suitable inert support are materials such as silica, magnesia, silicon carbide, alumina, aluminium silicate, magnesium silicate (steatite), or other silicates and mixtures thereof. The inert support may be in granular form or in pellet form, usually in the form of spheres, cylinders or rings. The coating of the active compound onto the inert support may be accomplished by spraying the aqueous or organic solution or slurry containing the ingredients and/or precursors on the support. This operation can be carried out in a heated drum, maintained at a temperature which is suitable for the evaporation of the solvent, for example in the range of 50 to 250 °C. The ratio between the amount of support and the amount of solution or slurry, and the amount of components dissolved in the solution or suspended in the slurry, are chosen so to reach the amount of active compound which is finally desired.

The final thermal treatment can be carried out in the heated drum mentioned above, or in a separate oven, or directly in the reactor where the selective oxidation of *o*-xylene, naphthalene or mixtures of the two to phthalic anhydride will take place. The treatment is carried out in air, or other suitable (non-reducing) atmosphere and at a temperature which is typically in the range 250–450 °C.

According to the invention, phthalic anhydride is prepared by oxidizing a hydrocarbon selected from the group consisting of *o*-xylene, naphthalene and mixtures of both in the gas phase at 340 to 400 °C with an oxygen-containing gas, preferably air, in a fixed-bed reactor in the presence of the catalyst of the invention. Advantageously, the oxidation reaction is carried out in a multitubular fixed bed reactor. The catalyst granules are filled into the tubes and the feed prepared by mixing air (or oxygen or any other oxygen-containing gas) with the hydrocarbon (i.e., *o*-xylene and/or naphthalene) is passed over the catalyst bed.

Preferably, the initial concentration (i.e., the concentration in the reactor feed) of the hydrocarbon is between 0.5 and 2 vol.%.
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The (gauge) pressure at the reactor inlet is advantageously slightly higher than atmospheric, preferably between 0.35 and 0.55 bar (absolute pressure: \approx 1.35–1.55 bar).

The following non-limiting examples and comparative examples describe preferred embodiments of the invention in relation to catalysts according to prior art:

Example 1 (Comparative Example)

- 5 V_2O_5 (7 wt.%) and Cs_2O (0.5 wt.%) were deposited on titania (anatase) having a surface area of $22.5 \text{ m}^2/\text{g}$. The catalyst was prepared by dissolution of 9.0 g of $(NH_4)VO_3$ in 2500 ml of hot (60–80 °C) deionized water under stirring. Then $CsNO_3$ (0.069 g) was dissolved in the same, hot solution. The titania (89.5 g) was dropped in the solution and the resulting slurry was loaded in a rotary evaporator to evaporate the solvent. The wet solid
- 10 was recovered and thermally treated using the following procedure, carried out in static air: Heating from room temperature to 150 °C at a heating rate of 10 K/min; isothermal step at 150 °C for 3 h; then further heating (10 K/min) till a temperature of 450 °C was reached. Final isothermal step at 450 °C for 5 h, and then cooling.

15 **Example 2**

The same procedure as described in Comparative Example 1 was used, except for the addition of 6.65 g of an aqueous tin oxyhydrate sol (Nyacol Co., grade SN15CG) having a tin content equivalent to 15 wt.% SnO_2 and a pH of 10.0. The tin content (as SnO_2) in the final catalyst was 1.0 wt.% with respect to the sum of SnO_2 , V_2O_5 and TiO_2 .

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Examples 3–6

The same procedure as described in Example 2 was used, except for the addition of 20 g, 26.7 g, 33.3 g, and 46.7 g of the SnO_2 sol. The tin content (as SnO_2) in the final catalysts was 3.0 wt.%, 4.0 wt.%, 5.0 wt.%, and 7.0 wt.%, respectively.

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Example 7 (Comparative Example)

The same procedure as described in Comparative Example 1 was used, leading to a catalyst with the same composition, except that the surface area of the titania was $18 \text{ m}^2/\text{g}$.

Example 8

The same procedure as described in Example 4, leading to the same final catalyst composition (i.e., 4.0 wt.% SnO₂), was used, except that the surface area of the was 18 m²/g and SnCl₄ was used as the Sn compound.

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Example 9 (Comparative Example)

The same procedure as described in Comparative Example 1, leading to a catalyst with the same composition, was used, except that the surface area of the TiO₂ (anatase) was 34 m²/g.

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Example 10

The same procedure as described in Example 4, leading to the same final catalyst composition, was used, except that the surface area of the TiO₂ (anatase) was 34 m²/g and the Sn compound was SnCl₄.

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Catalytic tests

The procedure for catalytic testing was the following: An upright tubular reactor made from stainless steel, with a diameter of 1.25 cm and 25 cm long was first loaded with 11.1 g of inert material (α -alumina, 30–60 mesh particles) and then with 0.23 g of catalyst mixed with 1.0 g of the inert material. The catalyst was shaped in granules having a diameter between 30 and 60 mesh. The feed consisted of *o*-xylene vapour (1 vol.%) in air, and the flow rate was such to have a residence time, measured at ambient conditions, of 0.3 s. The pressure was atmospheric.

20

The results obtained are summarized in Table 1. The selectivities to and yields of phthalic anhydride (PA) are given in mole%. It is evident from these results that:

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- (i) the addition of tin in the range examined (1–7 wt.% SnO₂) results in increased activity,
- (ii) the highest increase of activity is achieved when the amount of Sn is between about 3 and 5 wt.% SnO₂,
- (iii) that amount of Sn, and specifically an amount corresponding to 3–4 wt.% of SnO₂ also gives a higher maximum yield of PA as compared to a catalyst without tin.

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Table 1.

Example No.	T [°C]	Conv. [%]	Sel. PA [%]	Yield PA [%]
Comp. 1	327	26.4	61.1	16.1
	335	39.4	70.6	27.8
	347	61.5	77.0	47.4
	362	78.1	82.0	64.0
	369	86.4	83.3	72.0
	375	99.1	80.6	79.9
2	335	33.8	66.6	22.5
	347	76.1	75.7	57.6
	355	93.8	75.4	70.7
	362	97.4	73.8	71.9
3	315	20.5	54.1	11.1
	325	42.9	65.8	28.2
	335	84.9	78.1	66.3
	345	100	81.3	81.3
4	310	21.3	50.4	10.7
	320	36.2	68.6	24.8
	330	84.6	85.9	72.7
	340	99.2	85.0	84.3
5	315	23.9	54.1	12.9
	325	56.3	68.8	38.7
	335	93.1	73.2	68.1
	345	99.5	71.9	71.5
6	337	46.0	64.9	29.8
	349	75.4	77.4	58.4
	360	99.5	79.8	79.4
	368	100	77.0	77.0
Comp. 7	340	32.5	68.3	22.2
	350	63.8	78.5	50.1
	360	71.9	78.3	56.3
	370	80.9	78.6	63.6
8	330	18.0	48.9	8.8
	339	31.8	61.0	19.4
	355	83.2	79.9	66.5
	365	96.5	81.3	78.5
	371	100	81.5	81.5
Comp. 9	322	23.9	59.8	14.3
	326	46.3	71.0	32.9
	334	76.5	78.9	60.4
	342	89.3	80.7	72.1
	352	99.7	80.1	79.8
10	295	4.9	32.4	1.6
	310	9.6	40.7	3.9
	322	24.2	56.6	13.7
	334	95.8	79.6	76.2
	340	100	81.0	81.0